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Thesis

# THE COUPLING PERIODS OF SUBSTITUTED PHENYL-DIAZO COMPOUNDS WITH DIMETHYL ANILINE

by

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( B.S., St.John's University, 1932)

submitted in partial fulfilment of the requirements
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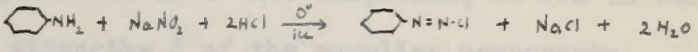
# THE COUPLING PERIODS OF SUBSTITUTED PHENYL-DIAZO COMPOUNDS WITH DIMETHYL ANILINE

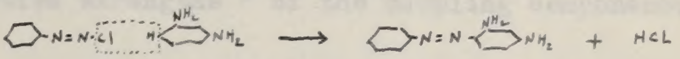
## The Problem

In preparing azo dyes, certain amines are first diazotized to give diazo compounds which in turn can be reacted with some amines or hydroxy compounds, usually called coupling components, to give respective dye-stuffs. Reactions of the former type are called diazotization reactions, and reactions of the latter type are called coupling reactions. A typical example of these two types of reactions is the preparation of chrysoidine, a yellow mono-azo dye, from phenyl-diazonium chloride and phenylene-diamine :

Diazotization reaction



Coupling reaction



The work of this thesis was carried out to evaluate the ease of coupling of a number of substituted phenyl-diazo compounds, and thereby to establish a series of these compounds with graded coupling periods. Coupling periods can be defined as the time required from the beginning to the end of the coupling reactions.

These coupling periods in specified conditions are usually referred to by industrial chemists as the " relative strengths " of these diazo compounds. Thus, diazotized mono-nitro and dinitro anilines are usually said to be " stronger " diazo compounds than those prepared from mono-chloro and di-chloro anilines respectively, since less time is necessary for the completion ( see p. 7 ) of their

coupling reactions. As a matter of fact, the term " relative strengths" which expresses the coupling periods of a series of diazo compounds is used purely for convenience and for comparison. The strengths of diazo compounds are said to be relative, because coupling periods vary with the reacting conditions, and fixed conditions must be specified for comparative results.

With the aid of the above statements, it may be understood that this investigation will furnish the relative strengths of a series of diazo compounds, as measured by their respective coupling periods under specified conditions. Future work is planned to study the " relative strengths " of some coupling components by determining their coupling periods with each of these graded diazo compounds. With the pre-determined strength of these latter compounds, we can in turn correlate the " relative strengths " of the coupling components.

The accumulation of data, as obtained by the above procedures, will be very valuable in an attempt to determine the mechanism of coupling reactions, which have been developed to such an extent that mechanisms as previously proposed are no longer found to be adequate for satisfactory explanations.

The present work has been merely the first step in the accumulation of the necessary data.

## Historical

A survery of the literature reveals that systematic estimation of the coupling periods of substituted phenyl-diazo compounds as planned for the present investigation, has not been carried out by any of the previous workers in this field.

Other investigators have been much interested in measuring coupling capacities in terms of their specific reaction rates. Thus, Goldschmidt[1] and his associates have measured the rate of formation of methyl orange from dimethyl aniline and p-diazo-benzene sulfonic acid. They kept the reacting substances at a constant temperature, and withdrew aliquot portions at given intervals of time. The amount of unaltered diazo compound was measured by the nitrogen evolved, when the solution was acidified and subsequently heated. Veley[2] has devised a tinctomatic method by which the rate of formation of certain azo compounds can be measured by estimating the amount of dye-stuff formed per unit time.

A more recent contribution on this phase of the problem is the investigation as carried out by Conant and Peterson[3] . They have measured colorimetrically the rate of reaction of five diazotized amines with certain phenols and naphthols in buffer solutions of constant ionic strength. Over a wide range of concentrations, the reaction corresponds to that calculated by the bi-molecular equation. Under the conditions investigated, they have shown that the rate of coupling is a simple function of the hydrogen ion activity of the buffer solutions. Purely for simplicity they assigned to each pair

---

1. Goldschmidt : Ber. 1902, 35, 3534.
2. Veley : J.C.S. 95, 1186, 1909.
3. Conant and Peterson : J.A.C.S. 52, 1220, 1930.

of diazo and coupling components they investigated certain empirical constants as " coupling values " which can be defined as the pH at which log K = 1.

A careful examination of their investigation will however reveal the fact that although their conclusions and assignment of coupling values are justifiable from the data obtained, it is not complete, since it was also observed that coupling was a function of the constitution of the reacting components. This latter part of the work is not thoroughly defined, and at the best, one is led to believe that the rate of reaction of a diazo compound is a function only of the nature of the phenols used.

## Outline of study

In the present connection, work has been planned to study the coupling periods of several diazo compounds with the same coupling component in a solution of definite acidity so that results can be correlated on a comparative basis. Phenyl-diazo compounds with different substituent groups have been used; and in order to account for the effect of the positions of these different substituent groups, isomeric compounds have been chosen for this work. The compounds selected for this investigation include diazo derivatives of ortho, meta, para, mono-nitro and mono-chloro anilines, as well as the isomeric compounds of di-nitro and di-chloro anilines.

The coupling periods have been measured by coupling each one of these substituted phenyl-diazo compounds with dimethyl aniline as a standard. The use of dimethylaniline as a standard coupling component is four-fold : First, it can be easily obtained and purified. Secondly, it is widely used as a coupling component. Thirdly, its coupling reactions with substituted phenyl-diazo compounds are practically quantitative and are free from complications due to side reactions. In the fourth place, the reaction with most diazo compounds proceeds readily.

With regard to the preparation of certain substituted phenyl-diazo compounds, special technique must be used, and consequently, two separate laboratory procedures have been employed. Mono-nitro and mono-chloro derivatives are rather easily obtained by diazotization of their respective amines under ordinary conditions as generally met

in cases of this sort; e.g. diazotization with 2 N.HCl and sodium nitrite at 5°C. On the other hand, the diazotization of dinitro-anilines is rather difficult unless effected by concentrated sulfuric acid and sodium nitrite, ( nitrosyl-sulfuric acid ) at a temperature slightly above room temperature ( 30° - 40°C ). Dichloro anilines can be diazotized with a 20 % solution of HCl and the appropriate amounts of sodium nitrite.

In order to connect up these two separate sub-series, bridge compounds such as nitro-chloro-anilines have been used. The latter have been diazotized under both conditions, and thereby served as a linkage to bind together these two sub-series on a comparative basis. Furthermore, in order to eliminate possible errors which might arise if comparisons of coupling periods were made with solutions of different acidities, the acidity of these diazo solutions of dichloro and dinitro derivatives has been reduced to the same value as that of mono-chloro and mono-nitro derivatives, by neutralizing the excess acid with appropriate amounts of base, before the coupling reaction was started.

It might also be stated here that excess sodium nitrite was used to insure complete diazotization, and it was decomposed by the addition of urea before coupling.

After the amines were diazotized and diazo compounds formed, the solutions were clarified by neutral charcoal to eliminate any diazo-amino bodies which might be present. Then the solutions were filtered, made up to the same volume, same acidity, and coupled with

a known excess ( 5 % ) of dimethyl aniline at a constant temperature ( 25°C ). Excess dimethyl aniline was used to insure complete coupling, and since equal amounts of excess were added in different baths, the relative coupling periods would remain constant.

The progress of the coupling reaction was easily followed by spotting the solution from time to time on a piece of filter paper, wetted with a solution of alkaline H-acid. As long as any diazo compound was present, an immediate red coloration appeared at the juncture of the two solutions. At the end of the reaction, when all of the diazo compound had been coupled, no color was obtained.

The sensitivity of alkaline H-acid as an indicator for diazo compounds has been estimated. A standard solution of 0.05 N. p-diazo -benzene sulfonic acid was prepared. On continual dilution and subsequent tests with alkaline H-acid, it was finally shown that alkaline H-acid was sensitive to the diazo compound for .002 g. in 500 mls. of solvent. This corresponds to one part of diazo compound to 250,000 parts of solvent; or, in other words, the end points as reached by alkaline H-acid represented at least 99.996 % of the total extent of coupling reactions.

The coupling periods have been recorded as the time from the beginning to the end of the coupling reactions.

## Experimental

### Preparation and Purification of Substituted Anilines

The author wishes to express his appreciation of the fact that all of the amines under investigation were generously supplied by the E.I.du Pont de Nemours & Co. Since some of the compounds were technical products, purifications were made in each case by either recrystallization or fractionation until definite melting points or boiling points were obtained.

Mono-nitro anilines were recrystallized from alcohol. The following constants were obtained : o-nitro-aniline M.P. 71.5° - 72°C., m-nitro-aniline M.P. 113.6° - 114°C., p-nitro-aniline M.P. 145° - 146°C.

o-chloro and m-chloro anilines were purified by fractionation; while p-chloro-aniline was recrystallized from hot water. The constants were : o-chloro-aniline B.P. 210° - 211°C., m-chloro-aniline B.P. 230°- 231°C., p-chloro-aniline M.P. 230.5° - 231°C.

Chloro-nitro-anilines were recrystallized from alcohol. The constants were : o-nitro-p-chloro-aniline M.P. 114.5° - 115°C., p-nitro-o-chloro-aniline M.P. 104° - 104.2°C.

2,4-dinitro-aniline was recrystallized from alcohol. The M.P. was 187.5° - 188°C.

Dichloro-anilines were recrystallized from ligroin. The following constants were obtained : 2,4-dichloro-aniline M.P. 63° - 63.2°C., 3,4-dichloro-aniline M.P. 71° - 72°C.

## A Review of Some Preliminary Experiments

### 1. Effect of Stirring

In order to estimate approximately the effect of stirring upon the coupling periods, three stirrers of varying speed were set up. With these, three samples of o-nitro-aniline were diazotized and coupled to equal amounts of dimethyl aniline according to procedure I ( cf. p. 18 ). As the following results showed ( Table I ), the speed of stirring in diazotization and coupling needed careful control, because it effected the respective coupling periods and was important from the point of view of occlusion of solid dye-stuff formed in the coupling baths. For later experiments, adjustments have been made so that the speed of stirring in various baths was 300 R.P.M., with a deviation of ±5 R.P.M.

Table I

Effect of Stirring upon the Coupling Period of o-Nitro-Phenyl-diazo Chloride with Dimethyl aniline.

Note : 0.1 mole of o-nitro aniline was diazotized with 200 mls. water, 128.2 mls. $1.95^{N}$ HCl ( ≙ 0.25 mole ) and 0.1 mole of Na $NO_2$ dissolved in 50 mls. water. The resulting diazo compound was coupled to 0.105 mole of dimethyl aniline at 23° - 25°C.

| | Quick Stirring (about 500 R.P.M.) | Medium Stirring (about 250 R.P.M.) | Slow Stirring (about 100 R.P.M.) |
|---|---|---|---|
| Coupling Period | 1 hr. | 1 hr. 20 mins. | 2 hrs. |

## 2. Effect of Temperature

This effect was observed when two series of runs were carried out in different room temperatures. Table II shows the Coupling periods at these two temperature.

### Table II

Effect of Temperature upon the Coupling Periods of substituted Phenyl-diazo Compounds with Dimethyl aniline.

Note : 0.1 mole of amine was diazotized with 200 mls. water, 128.2 mls. 1.95"HCl ( ≙ 0.25 mole ) and 0.1 mole of $NaNO_2$ dissolved in 50 mls. water. The resulting diazo soalution was not filtered, but coupled to 0.105 mole of dimethyl aniline .

| | Coupling Periods | |
|---|---|---|
| | Temp. 25°-25.5°C. | Temp. 17°-18°C. |
| o-nitro-phenyl-diazo-chloride | 50 mins. | 3 hrs. |
| m-nitro-phenyl-diazo-chloride | 2 hrs. 15 mins. | 5 hrs. 10 mins. |
| p-nitro-phenyl-diazo-chloride | 3 hrs. 35 mins. | 6 hrs. 20 mins. |

The effect of temperature upon the coupling reactions was tremendous. Evidently, when the temperature was decreased, the coupling periods were greatly lengthened. For later determinations, a water-bath has been used to keep the temperature of the coupling bath as near 25°C. as possible with a deviation of ±1 C.

### 3. Effect of the Amount of Acid Present in the Coupling Bath

It is a common knowledge that reaction velocity varies with medium. This comparison of the amount of acid present in the coupling bath was carried out to estimate the effect of the varying acidities. Table III shows some of the comparisons at 20°C.

Table III

Effect of the Amount of Acid Present upon the Coupling Periods of substituted Phenyl-diazo Compounds with Dimethyl aniline.

**Note** : In each case, 0.1 mole of amine was used, appropriate amounts of HCl added, and diazotized with 0.1 mole of $NaNO_2$ dissolved in 50 mls. water. The diazo solution was not filtered. Coupled to 0.105 mole of dimethyl aniline as usual. Temp 20°C. Volume constant = 500 mls.

| | Acidity I | Acidity II |
|---|---|---|
| | 128.2 mls. 1.95 N HCl<br>( ≏ 0.25 mole ) | 256.4 cc. 1.95 N.HCl<br>( ≏ 0.50 mole ) |
| m-nitro-phenyl-diazo chloride | 2 hrs. 15 mins. | 2 hrs. 30 mins. |
| p-nitro-phenyl-diazo-chloride | 4 hrs. 40 mins. | 4 hrs. 45 mins. |

The variation of the amount of acid present was thus shown to produce but a very slight effect on the length of the coupling period.

### 4. Effect of Different Dilutions of the Same Amount of Acid Present in the Coupling Bath.

Another series of experiments was carried out to estimate the dilution factor of the amount of acid present. From Table IV., as shown below, the results indicated that a moderate change in the dilution of the acid produced but a very slight change in the length of the coupling period.

Table IV.

Effect of Different Dilutions of the Same Amount of Acid Present upon the Coupling Periods of substituted Phenyl-diazo Compounds with Dimethyl aniline.

Note: In each case, 0.1 mole of amine was diazotized with 200 mls. water, 128.2 mls. 1.95 N.HCl ($\doteq$ o.25 mole), and o.1 mole $NaNO_2$ dissolved in 50 mls. water. The resulting diazo solutions were not filtered, but the volumes were made up according to the following dilutions. Coupled to 0.105 mole of Dimethyl aniline as usual. Temp. 20° C. Amount of acid constant.

| | Dilution I<br>Vol. before coupling<br>500 mls. | Dilution II<br>Vol. before coupling<br>800 mls. |
|---|---|---|
| m-nitro-phenyl-diazo chloride | 2 hrs. 15 mins. | 2 hrs. 20 mins. |
| p-nitro-phenyl-diazo chloride | 4 hrs. 40 mins. | 4 hrs. 50 mins. |

### 5. Effect of Diazo-amino Compound Formation during diazotization

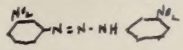
As we generally know, diazo-compounds when they are first diazotized will react with the undiazotized amines to form diazo-amino compounds as side-products; thus

$$R\cdot N_2Cl \; + \; R\cdot NH_2 \rightleftarrows R\cdot N{:}N\cdot NH\cdot R \; + \; HCl$$

Since it has been the aim of this work to measure the coupling periods of diazo compounds, and not the side product, the formation of such diazo-amino compounds would effect the percentage yield of the actual diazo compounds, and hence the coupling periods of these latter compounds with dimethyl aniline would also be affected. For this reason, it was planned right at the start to carry out these coupling reactions in a fairly strong acidic medium, in which this side-reaction can be eliminated to a great extent, because it is reversible, and the reverse reaction is favored in a more strongly acid medium.

Although due consideration had been taken of the factors already discussed, some preliminary runs did not check with each other. It was natural, then, to study the extent of this side-reaction and also the effect of the presence of the diazo-amino compound on the coupling period.

After repeated determinations, it was finally observed that during the diazotization, a small amount of diazo-amino compound was formed. In these cases, some floculent precipitate appeared after diazotization. In the case of m-nitro-aniline, this precipitate was filtered off and completely washed. A very small portion of it was dried carefully ( dry diazo-amino compound is also explosive ) and

the melting point taken. The melting point was 160° -163° C, showing that the precipitate after diazotization was a mixture of undiazotized m-nitro-aniline ( pure m-nitro-aniline M.P. 114°C ) and the corresponding diazo-amino compound ( pure  M.P. 194°c.). The diazo-amino compound was obtained by extracting the precipitate with acetone and subsequent precipitation with water. It was purified by redissolving in acetone and precipitation with water. The product obtained had the melting point 193° - 194°C. On the other hand, the residue after acetone extraction contained some impurities together with a trace of undiazotized m-nitro-aniline, which was obtained by extracting the residue with alcohol and subsequent precipitation with water. It was also purified by redissolving in alcohol and precipitation with water. The product had the melting point 113° - 114° C.

It might also be stated here that the precipitates formed in solution after diazotization were first suspected to contain also some of the diazo compound.But it was shown that the precipitates, after complete washing, did not give a color test with H-acid. This indicated very clearly that they were free from diazo compounds. All diazo compounds are soluble in water, with the exception of those amines which have sulphonic acid groups as substituents.

Since the amounts of these diazo-amino bodies were small, the next logical step to be taken was to ascertain whether or not the presence of them would effect the coupling periods of the normal diazo compounds. In Table V., two cases were set up. In one case, the amine~~s~~ was diazotized and coupled to dimethyl aniline in accordance with the procedure as taken in previous experiments. In another, the amine was

diazotized as usual, but the diazo solution was clarified with charcoal as an adsorbing agent and filtered; then the filtered solution was used for coupling with dimethyl aniline.

### Table V.

Effect of Diazo-amino compound Formation upon the Coupling Periods of substituted Phenyl-diazo Compounds with Dimethyl aniline.

Note : In each case, 0.1 mole amine was diazotized with 200 mls. water, 128.2 mls. of 1.95 N.HCl (≙ 0.25 mole ) and 0.1 mole $NaNO_2$ dissolved in 50 mls. water. In case I, the diazo solution was coupled to Dimethyl aniline as usual. In case II, the diazo solution was clarified with neutral charcoal and filtered; then the filtered solution was coupled with Dimethyl aniline.

| | Unfiltered diazo solu. | filtered diazo solu. |
|---|---|---|
| o-nitro-phenyl diazo chloride | 50 mins. | 35 mins. |
| m-nitro-phenyl-diazo chloride | 2 hrs. 15 mins. | 2 hrs. |
| p-nitro-phenyl-diazo chloride | 3 hrs. 35 mins. | 2 hrs. 30 mins. |

An inspection of the above coupling periods at once reveals that the presence of diazo-amino bodies lengthened the coupling periods of diazo compounds, and they should be filtered off with neutral charcoal. This consideration was neglected in previous runs.

## 6. Technique Involved in Diazotizing the Amines

In considering the diazo-amino compound formation in coupling baths, we can say that it was due to the incompleteness of diazotization. And since the amines were not completely diazotized, a very small percentage of them must be unconverted which reacted subsequently with the already transformed diazo compounds to form diazo-amino bodies.

Later determinations were carried out with the use of excess $NaNO_2$ ( 0.102 mole of $NaNO_2$ to 0.1 mole of amine ). This was to insure that all of the amine was diazotized. Excess nitrite in the diazo solution was later removed by adding a concentrated solution of urea, one drop at a time until no trace of nitrous acid could be detected by KI-starch paper. The use of urea to remove the nitrite in excess was in accordance with the following equation :

$$2\ HONO + OC\begin{matrix}\diagup NH2\\ \diagdown NH2\end{matrix} \longrightarrow 2\ N_2 + CO_2 + 3\ H_2O$$

The diazo solution was not effected during the above process, and could be coupled with dimethyl aniline as usual.

In the opinion of the writer, proper conditions of diazotization, even with the use of excess sodium nitrite, can only be attained through training and long practice.

It has been stated that the formation of diazo-amino compounds as side-products in minor quantities was due to the incompleteness of diazotization. In order to decrease the extent of diazo-amino compound$ formation and to increase the yield of diazo compound, it was decided to have an excess sodium nitrite in the solution at all times during

the diazotization. Perhaps an example will make this clearer. In the diazotization of mono-nitro anilines, the amines absorb the nitrite solution rather readily at the beginning so that about 80 % of the latter should be added immediately. Toward the end of the diazotization, however, the nitrite solution was added slowly. The presence of free nitrous acid can be easily traced with KI-starch paper.

Since loss may be incurred by incomplete diazotization and filtration with neutral charcoal, a method was devised by which the diazo solution could be analyzed. This was done by coupling the diazo solution to a known excess of dimethyl aniline as usual, and back titrating the unreacted dimethyl aniline in a sodium acetate medium with a standard solution of p-sulphonic phenyl-diazo chloride. Since the coupling reactions between dimethyl aniline and the diazo compounds concerned are quantitative, the amount of dimethyl aniline obtained in back titration as compared with the initial excess would furnish data necessary to calculate the percentage yield of the diazo compounds during the process of diazotization.

Since the back titrations showed a consistently high yield ( over 90 % ) of the diazo compounds in all cases, the coupling periods recorded were then assumed to be acceptable on a comparative basis.

## Final Procedure developed from Preliminary Experiments

It should be realized that those factors as outlined above were investigated one at a time.Hence, the results as tabulated in different tables up to this point were only justifiable from the point of view of their separate effects. They were in no way to indicate that represent~~ed~~ing the actual coupling periods of diazo compounds as can be correlated ona comparative basis. The final procedure was developed from a consideration of the above factors.

### I. For easily diazotized amines, including mono-nitro and mono-chloro aniline.

### Typical Procedure

0.1 mole of p-nitro-aniline , together with 200 mls. of water and 128.2 mls. 1.95 N HCl ( $\approx$ 0.25 mole),was stirred for a few minutes at 25°C. Then the solution was cooled with ice to 5° - 10° C. 0.102 mole of $NaNO_2$ dissolved in 50 mls. of water was added to the above solution rapidly at first -- about 80 % at once; while the remainder was added in more slowly , an excess of nitrite being always kept present as shown by a blue coloration on KI-starch paper. The excess was maintained for at least 15 minutes after all the nitrite was added. An instaneous blue color appeared if excess nitrite was present. Temperature 5° - 10° C. Five grams of neutral charcoal were added for clarification, and the solution filtered. If any excess nitrous acid was present ( as most of all cases did ) , it was decomposed by adding a fairly concentrated solution of urea, one drop at a time, until the end point was reached when an instantaneous blue test with KI-starch paper was no longer obtained.

( most diazo compounds developed a faint violet color with KI-starch ). Then the diazo solution was diluted to about 500 mls., and the temperature raised to 25° C. The coupling reaction was carried out by adding from a burette all at once a definite volume of dimethyl aniline corresponding to 0.105 mole. Efficient stirring at a constant speed ( 300 R.P.M. ) was kept at all times during the coupling reaction, which was continued at 25° C. until no further positive test for diazo compound was obtained,when spotted with alkaline H-acid solution. A positive test was a red coloration at the juncture of the two solutions when they were spotted on a piece of filter paper. On the other hand, an excess of dimethyl aniline was shown to be present, as a brownish color appeared at the rim of the spot when touched with a solution of p-nitro-phenyl-diazo chloride. The coupling period ( in time ) as from the beginning to the end of the coupling reaction was measured.

After the coupling reaction was finished , the unreacted dimethyl aniline was back titrated with a .05 N. solution of p-sulphonic phenyl-diazo chloride. The yield of the diazo compound which actually coupled was then calculated.

## II. For amines which are difficult to be diazotized

### a. For dinitro-anilines, using concentrated sulfuric acid.

Typical Procedure

0.102 mole of $NaNO_2$ was added slowly to 80 mls. of conc.$H_2SO_4$, stirrig continuously. Temperature about 30 C°. The solution was heated up to 60° C, and cooled back to 30° C.( this process was to make nitrosyl-sulfuric acid). 0.1 mole of 2,4-dinitro-aniline was then added to the solution. Stirred for 3 hrs. at 30°-40° C. At the end of that time, the solution was poured on to 80 grams of ice. Five grams of neutral charcoal were added, while stirring, and the solution filtered. Surrounded with ice, the filtrate was neutralized with an appropriate amount of caustic soda ( in a conc. solution ) in order to reduce it to the right acidity. Any $Na_2SO_4$ that was precipitated was filtered and thoroughly washed. The solution was then made up to one liter. Any excess nitrous acid present was decomposed by urea solution as usuall, and the temperature raised to 25° C. The coupling reaction was carried out by adding all at once from a burette a volume of dimethyl aniline corresponding to 0.105 mole. The coupling reaction was continued with stirring at 25° C. until a negative test for diazo compound was obtained with alkaline H-acid. The coupling period (in time) as from the beginning to the end of the couplig reaction was measured.

After the coupling reaction was completed, the unreacted dimethyl aniline was back titrated with a 0.05 N. solution of p-sulphonic phenyl-diazo chloride. The yield of the diazo compound which actually coupled was then calculated.

### b. For Dichloro-anilines, using 20 % hydrochloric acid.

### Typical Procedure

0.1 mole of 2,4-dichloro-aniline was broken up into fine particles by screening through a 20-mesh sieve, and added to 20 % solution of HCl. The mixture was heated to 75° C for one and half-hour. Cooled, with stirring, to 30° C, and added ice until temperature was below 10° C. The solution was diazotized by adding slowly 0.102 mole of $NaNO_2$ , which was dissolved in 50 mls. of water. The resulting diazo solution was pale yellow, clarified with charcoal, and filtered. Any excess nitrous acid present was decomposed by urea solution. The diazo solution was finally made up to 500 mls. The coupling reaction was carried out as usual by adding all at once 0.105 mole of dimethylaniline. The coupling reaction was continued with stirring at 25°C. until a negative test for diazo compound was obtained with alkaline H-acid. The coupling period ( in time ) as from the beginning to the end of the coupling reaction was recorded.

After the coupling reaction was completed, the unreacted dimethyl aniline was back titrated with a 0.05 N. solution of p-sulphonic phenyl-diazo chloride. The yield of the diazo compound which actually coupled was calculated.

Note: The acidity of this procedure for dichloro-anilines was the same as Procedure I, only a more concentrated solution of HCl was used. The results were directly comparable to those mono-nitro and mono-chloro anilines as carried out with Procedure I, and no neutralization with caustic soda was necessary.

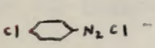
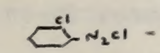
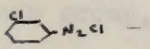
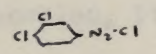
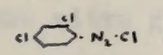
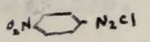
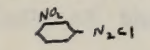
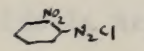
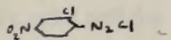
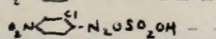
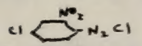
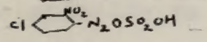
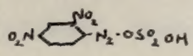
Tabulated Data :

The following ( Table VI. ) summarizes the coupling periods of some substituted phenyl diazo compounds with dimethyl-aniline. Due consideration has been made for the different factors as outlined in the preliminary work.

Table VI

Coupling Periods of Substituted Phenyl-diazo Compounds with Dimethylaniline

increasing strength of Coupling

| Substituted Phenyl-diazo compounds | Coupling Periods | % yield of diazo cpd. from back titration | Specifications |
|---|---|---|---|
|  | 238 hrs. | 98 % | # Procedure I |
|  | 120 hrs. | 97 % | # Procedure I |
|  | 55 hrs. | 97 % | # Procedure I |
|  | 14 hrs. 10 mins. | 94 % | * Procedure IIb |
|  | 14 hrs. | 93 % | * Procedure IIb |
|  | 2 hrs. 30 mins. | 95 % | * Procedure I |
|  | 2 hrs. | 95 % | * Procedure I |
|  | 45 mins. | 96 % | * Procedure IIb |
|  | 34 mins. | 90 % | * Procedure I |
|  | 31 mins. | 95 % | * Procedure IIa |
|  | 30 mins. | 89 % | * Procedure I |
|  | 29 mins. | 96 % | * Procedure IIa |
|  | 20 mins. | 93 % | * Procedure IIa |

# result of one trial.

* result of two trials.

## Discussion of Results

An examination of the results as summarized in Table VI. will at once reveal that the coupling periods of substituted phenyl-diazo compounds under identical conditions are functions of their constitution. The dominant factors are the nature and position of the substituted groups.

From the diazo compounds included in this work, the nitro group have been observed to impart to their respective diazo compounds greater coupling strength than chloro groups. Thus, the diazo derivatives of the mono-nitro anilines have shorter coupling periods than those of mono-chloro and di-chloro anilines. Even those derivatives of chloro-nitroanilines, in which a nitro group is present along with a chloro group, the coupling periods were greatly shortened. In this connection, it would also be interesting to note that the influence of the nitro group is so overwhelming that the effect of chloro-group is neglible. This can be seen very clearly by comparing the coupling periods of the following three compounds : 2,4-dichloro-phenyl-diazo-chloride 14 hrs., o-nitro-phenyl-diazo chloride 45 mins.,o-nitro-p-chloro-phenyl-diazo chloride 30 mins.. Apparently, the substitution of a nitro group instead of a chloro group in the ortho position of 2,4-dichloro-phenyl-diazo chloride as in the case of o-nitro-p-chloro-phenyl-diazo chloride has greatly decreased the coupling period from 14 hrs. to 30 mins.

With regard to the influence exerted by the different positions of these substituent groups in phenyl-diazo compounds, irregularities have been observed. In the series of mono-chloro-phenyl-diazo chlorides, the order of increasing strength as observed was p-chloro, o-chloro,

m-chloro-. In the series of dichloro-anilines, the difference of coupling periods as caused by varying positions was so neglibly small as cannot be profitably stated. In the series of mono-nitro-phenyl-diazo chlorides, the order of increasing strength was p-nitro, m-nitro, o-nitro. In the series of chloro-nitro-phenyl-diazo chlorides, the difference due to positions of substituent groups was also small; but there was an indication that the o-nitro-p-chloro-phenyl-diazo chloride was a little stronger than p-nitro-o-chloro-phenyl-diazo chloride. Di-nitro-phenyl-diazo compound was the strongest of all the above compounds.

## Summary

1. Several experimental factors influencing the coupling periods of phenyl-diazo compounds have been carefully investigated :
   - a. Stirring -- An increase in speed of stirring brought about faster coupling.
   - b. Temperature -- An increase in temperature hastened the coupling reaction. .
   - c. Ammunt of acid present in the coupling bath -- The amount of acid present in the coupling bath has caused only a small difference in the coupling period.
   - d. Dilution of the same amount of acid Present -- A moderate change in the dilution of the acid produced but a very slight change in the length of the coupling period.
   - e. Diazo-amino compound formation during diazotization -- The diazo-amino formation during diazotization interfered with the coupling periods, and was eliminated by filtering the diazo solution with neutral charcoal.
   - f. Technique in diazotizing the amines -- The technique of proper diazotization was attained through training and long practice. The essentials were stated.
2. After taking the above factors intoconsideration, the coupling periods of 11 substituted phenyl-diazo compounds with dimethyl aniline were measured by using alkaline H-acid as an indicator.
3. These coupling periods arranged in gradation gave the " relative strength of coupling " of these substituted phenyl-diazo compounds.
4. The coupling periods of substituted phenyl-diazo compounds as

carried out in identical conditions were found to be functions of their constitution. And the dominant constitutional factors were the nature and position of the substituent groups in their respective compounds.

5. Within the scope of this investigation, nitro groups were found to impart greater coupling strength to diazo compounds than chloro groups.
6. With regard to the effect of different positions as occupied by the substituent groups, irregularities in coupling periods were observed.

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